ALLYL SUCROSE: A NEW INDUSTRIAL PRODUCT

A Sucrose Derivative Which Gives Promise of Useful Application in Industrial Use as a Coating, an Adhesive and an Impregnant

By P. L. Nichols, Jr., and E. Yanovsky

Eastern Regional Research Laboratory*
Philadelphia, Pennsylvania

THE most important industrial use for sucrose at present is the production of alcohol by yeast fermentation. To the best of our knowledge the only derivative of sugar, made on a limited industrial scale, is sucrose octaacetate, which is used as a plasticizer, as an ingredient of lacquers and adhesives, and for denaturing alcohol. Various other uses for sugar and sugar derivatives have been suggested from time to time.'·*

In this paper the preparation and properties of allyl ether of sucrose, or allyl sucrose, are described. It is shown, furthermore, that this material has potential uses as a resistant, protective, and decorative coating, as an adhesive, and as an impregnant for wood, paper, and similar materials. The broader implications of this work on the polymerization of sucrose derivatives are discussed briefly.

The preparation of allyl sucrose (pentaallyl sucrose) was reported by Tomecko and Adams,'⁰ who treated sucrose with an excess of allvl bromide in the presence of 10% sodium hydroxide solution. Frey prepared allyl sucrose by a somewhat similar method. Our attempts to prepare allyl sucrose in good yields by the procedure described by Tomecko and Adams were unsuccessful. Under the conditions of the experiment, the 10% alkali recommended by them hydrolyzed allyl bromide rapidly; at higher concentrations the rate of hydrolysis was reduced considerably.* Fifty percent alkali proved to be a more satisfactory medium, both from the standpoint of yield and extent of subsitution. Tomecko and Adams obtained allyl sucrose with five allyl groups, whereas our procedure gave a product with seven allyl groups. From a practical standpoint, Tomecko and Adams, and Frey apparently overlooked a very important property of allyl sucrose and the allyl ethers of other carbohydrates, namely, their ability, through oxidation and polymerization, to change into insoluble and infusible resins.

Methods of Preparation of Allyl Sucrose

Laboratory Method.'— Sucrose (42.8 g.)

*One of the laboratories of the bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

was suspended in 176 grams of 50% aqueous sodium hydroxide in a three-neck flask equipped with a condenser. dropping funnel, and stirrer. Allyl bromide (242.0 g.) was added dropwise to the well-stirred reaction mixture over a period of four to five hours while the temperature was maintained at 70-75°. The reaction was then allowed to proceed for an additional hour, whereupon the product was extracted with ether and washed free of alkali. The volatile impurities were then removed by steam distillation.

Allyl sucrose prepared in this manner was a heavy light-yellow liquid and contained an average degree of substitution of about seven allyl groups. The yield was 68% of the theoretical amount. The high-boiling product was distilled in a molecular still (Hickman type) at a pressure of five microns and a bath temperature of 190-192°. Analysis of the distillate showed that the product corresponded roughly to heptaallyl sucrose, indicating little, if any, fractionation during the process of distillation. Properties:

n_D^{20} 1.4912; d_4^{20} 1.1071; viscosity at 25°, 792.5 centipoises; $[a]_D^{25}$ +50.5°; molecular refraction, 163.0 (calculated for heptaallyl sucrose, 164.8); allyl content, 44.3% (calculated for heptaallyl sucrose, 46.2%).

Preparation of Allyl Sucrose with Allyl Chloride. — For large-scale preparation of allyl sucrose, it would be necessary to use allyl chloride, which is less expensive. Since allyl chloride boils at a relatively low temperature (45°), the reaction must be conducted in an autoclave. One kilogram of sucrose is added to 3.75 kgs. of 50% sodium hydroxide and 3.5 kgs. of allyl chloride in a 2-gallon steam-jacketed autoclave equipped with a stirrer. The autoclave should be constructed or lined with a material which is resistant to alkali and allyl chloride, such as Monel metal. The reaction mixture is heated to 85°. Heating during initial stages of the reaction must be carefully controlled, since the reaction is exothermic and a rise in temperature might cause considerable increase in pressure. After heating and stirring for four to five hours, the reaction mixture is washed with water to re-

move salt and excess alkali. The resulting material is then steam distilled to remove volatile constituents, such as allyl chloride, allyl ether, and allyl alcohol. The sirupy allyl sucrose is then separated from the aqueous layer and dried over sodium sulphate. The yield is about 60% of the theoretical. This method requires a large excess of allyl chloride and alkali. Further work is necessary to improve the yield and to establish the optimum conditions for the reaction.

Preparation of Octaallyl Sucrose. — The above-described preparations of allyl sucrose are adequate for all practical applications. It might be of interest, however, to know that almost completely substituted allyl sucrose (octaallyl sucrose) was prepared in the following manner: two hundred grams of roughly heptaallyl sucrose (containing 3.5% hydroxyl) were placed in a 500-cc. three-neck flask equipped with a stirrer, condenser, and dropping funnel. After the surrounding oil bath was heated to 105°, 12.3 grams of sodium were added in small pieces to the stirred mixture in the flask over a period of 25 minutes. The reaction mixture was heated and stirred for an additional two hours. The temperature of the oil bath was then lowered to 85°, 71 cc. of allyl bromide was added dropwise over a period of 15 minutes and stirring at this temperature was maintained for 2 hours. After the reaction mixture has cooled to room temperature, a small quantity of alcohol was added to insure complete reaction of the sodium. The product was then steam distilled to remove volatile impurities, washed with distilled water, and dissolved in ether. The ether solution was washed with water and dried over sodium sulphate, and the ether was removed by distillation. The sirupy residue was distilled at 1-micron pressure in a Hickman still. Octaallyl sucrose has the following properties:

n_D^{20} 1.4822; d_4^{20} 1.0618;

Molecular refraction;178.0 (calculated for octaallyl sucrose, 178.4); allyl content, 48.5% (calculated for octaallyl sucrose 49.6%), which corresponds to 7.7 allyl groups; free hydroxyl, 0.37%, which corresponds to 7.9 allyl groups.

Polymerization of Allyl Sucrose

When allyl sucrose is exposed to air or oxygen, particularly at elevated temperature, the physical changes observed are an increase in density, refractive index, and viscosity, accompanied by gelation and further hardening to an insoluble, infusible, transparent resin. The change in viscosity with time (Table 1 and Figure 1) is characteristic of the polymerization of a polyfunctional monomer, with the formation of a three-dimensional network of primary valence bonds.

Table 1.

Polymerization of Allyl Sucrose [a]

Allyl Sucrose		Allyl Sucrose plus Co Naphthenate [c]	
Time hours	Viscosity centistokes at 97°	Time hours	Viscosity centistokes at 97°
0	10.0	0	9.7
0.5	12.1	0.5	26.7
1.0	15.2	1.0	126.8
1.5	20.2	2.0	∞ [b]
2.0	29.0		
2.5	44.0		
3.0	78.8		
3.5	157.1		
4.5	∞ [b]		

[a] The reaction was conducted and the viscosity measured in a modified Ostwald pipet, through which oxygen was passed at a uniform rate.
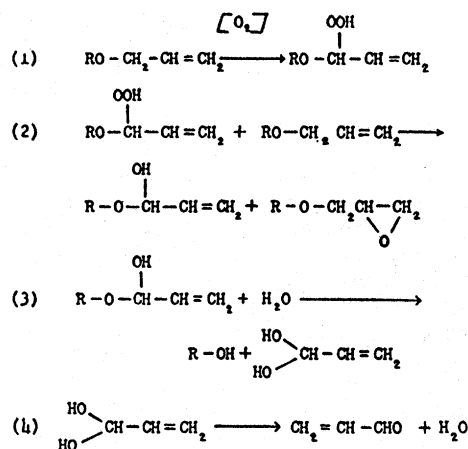
[b] During this measurement, the material gelled in the tube.

[c] The allyl sucrose-cobalt naphthenate mixture contained 0.1% cobalt

The agents which catalyze the polymerization of allyl sucrose most effectively are metallic salts of organic acids; among these, cobalt naphthenate is very effective (Table 1). Ultraviolet radiation likewise catalyzes this polymerization. It is interesting to note that organic peroxides, such as benzoyl peroxide or tertiary butyl hydroperoxide, are relatively ineffective as catalysts for this process. Either of these reagents, even in concentrations as high as 5%, causes little change in viscosity of allyl sucrose when the mixture is heated at 80° to 100° for several hours. Inhibition of polymerization of allyl sucrose can be effected with alkalies or organic bases. Allyl sucrose normally gels in about three hours when heated at 100° in the presence of oxygen, but the same conditions did not produce any increase in viscosity when 2% of triethylene tetramine was added.

Besides the physical changes observed during the polymerization of allyl sucrose, a number of chemical reactions take place. A distinct test for peroxide is obtained. Formation of epoxides is detected by the method of Nicolet and Poulter.[2] Also, a strong odor of acrolein accompanies the oxidation and polymerization of allyl sucrose. The acrolein can be distilled off and identified by means of its 2,4-dinitrophenyl-hydrazone. If we accept the theory of Criegee, Pilz and Flygare[3] and of Farmer and Sundralingam[4] on the autoxidation of olefinic compounds, there is a rather simple explanation for the positive peroxide and epoxide test and the formation of acrolein. The following equations would represent the course of the reaction:

$$(1) \quad RO-CH_2-CH=CH_2 \xrightarrow{[O]} RO-\overset{\overset{\displaystyle OOH}{|}}{C}H-CH=CH_2$$

$$(2) \quad RO-\overset{\overset{\displaystyle OOH}{|}}{C}H-CH=CH_2 + RO-CH_2\,CH=CH_2 \longrightarrow$$
$$R-O-\overset{\overset{\displaystyle OH}{|}}{C}H-CH=CH_2 + R-O-CH_2CH\overset{\displaystyle O}{\overset{\displaystyle \diagup\diagdown}{-}}CH_2$$

$$(3) \quad R-O-\overset{\overset{\displaystyle OH}{|}}{C}H-CH=CH_2 + H_2O \longrightarrow$$
$$R-OH + \overset{HO}{\underset{HO}{>}}CH-CH=CH_2$$

$$(4) \quad \overset{HO}{\underset{HO}{>}}CH-CH=CH_2 \longrightarrow CH_2=CH-CHO + H_2O$$

The first step shows formation of the hydroperoxide at the α-methylenic carbon which in this case should be especially reactive, since it is both adjacent to an ether oxygen and in α-position to a double bond. The second step shows decomposition of the peroxide according to the scheme suggested by Farmer and Sundralingam, in which the hydroperoxide oxidizes a double bond with the formation of an epoxy group. These two equations represent the application of Farmer's ideas to our compound. The hydroxy compound formed as a result of step two is a hemiacetal, which would be readily hydrolyzed if a trace of water were present. It is evident from equations 3 and 4 that a trace of water is all that is necessary for complete hydrolysis of any amount of hemiacetal formed, and according to Farmer's theory and our own observations water is formed during oxidations of this type.

It would be more difficult to understand how the formation of acrolein could take place should the initial peroxide have the

cyclic structure $-\overset{C}{\underset{O}{\diagdown}}\overset{C}{\underset{O}{\diagup}}-$
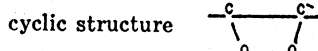
as suggested by Engler.[5] The formation of epoxy groups in the above-suggested scheme of oxidation and the well-known ease with which epoxy compounds polymerize led us to suspect that this group plays an important role in the polymerization and cross-linkage of allyl sucrose.

Potential Applications of Allyl Sucrose

From the nature of polymerized allyl sucrose it is at once apparent that this material might be extremely valuable for coating wood, metal, and other surfaces which might be subject to action of solvents, oils, and heat. While sirupy allyl sucrose is soluble in almost all organic solvents, a properly cured film of this material is insoluble in all organic solvents tested, withstands immersion in hot oils, and is resistant to heat up to 200°C. The coating possesses high gloss and extreme hardness but at the same time sufficient flexibility to make it desirable for many applications. Besides, if necessary, allyl sucrose can be modified with various plasticizers and other resins.

The method of application of allyl sucrose can be varied to suit particular needs. One of the methods is to polymerize it partially ("body") by passing air or oxygen through the heated liquid. If this process is stopped before the gelation point, the material will easily disperse in most organic solvents or mixtures of solvents and can be applied either by brushing or spraying. On evaporation of the solvents, the somewhat tacky coating dries and when heated for 2 or 3 hours at 80° to 100°C. becomes completely insoluble. The tackiness disappears more quickly, and the process of insolubilization takes place in less time and at lower temperature if a small amount of cobalt naphthenate is added (0.1% or less cobalt, based on weight of allyl sucrose). The tackiness can be eliminated, and complete insolubility of the film can be achieved in 3 or 5 hours at room temperature by treating the film with vapors of sulphur chloride or sulphur dichloride.

Allyl sucrose has good adhesive properties and might find use as a waterproof adhesive for laminates. Owing to its transparency, it might serve as an adhesive for glass. Among other applications, coating and impregnating paper, textiles, and other materials with allyl sucrose for water and grease proofing and increasing the tensile strength should be considered. Some promising work has been done along these lines, but considerably more work will be required before more positive statements can be made.

Besides the allyl sucrose described here, β-methallyl and β-chlorallyl ethers of sucrose have been prepared. They behave essentially in the same manner as allyl sucrose but apparently have no advantage over it.

Although only one type of useful derivatives of sucrose has been described here, this work opens a new field of research, namely, the preparation of polymerizable derivatives of sucrose. One would expect that an unsaturated monomer of sucrose with its high degree of functionality would rapidly polymerize with excessive cross-linkage, resulting in a very brittle, perhaps entirely insoluble, and therefore useless substance. The utility of allyl sucrose gives promise that other sucrose monomers

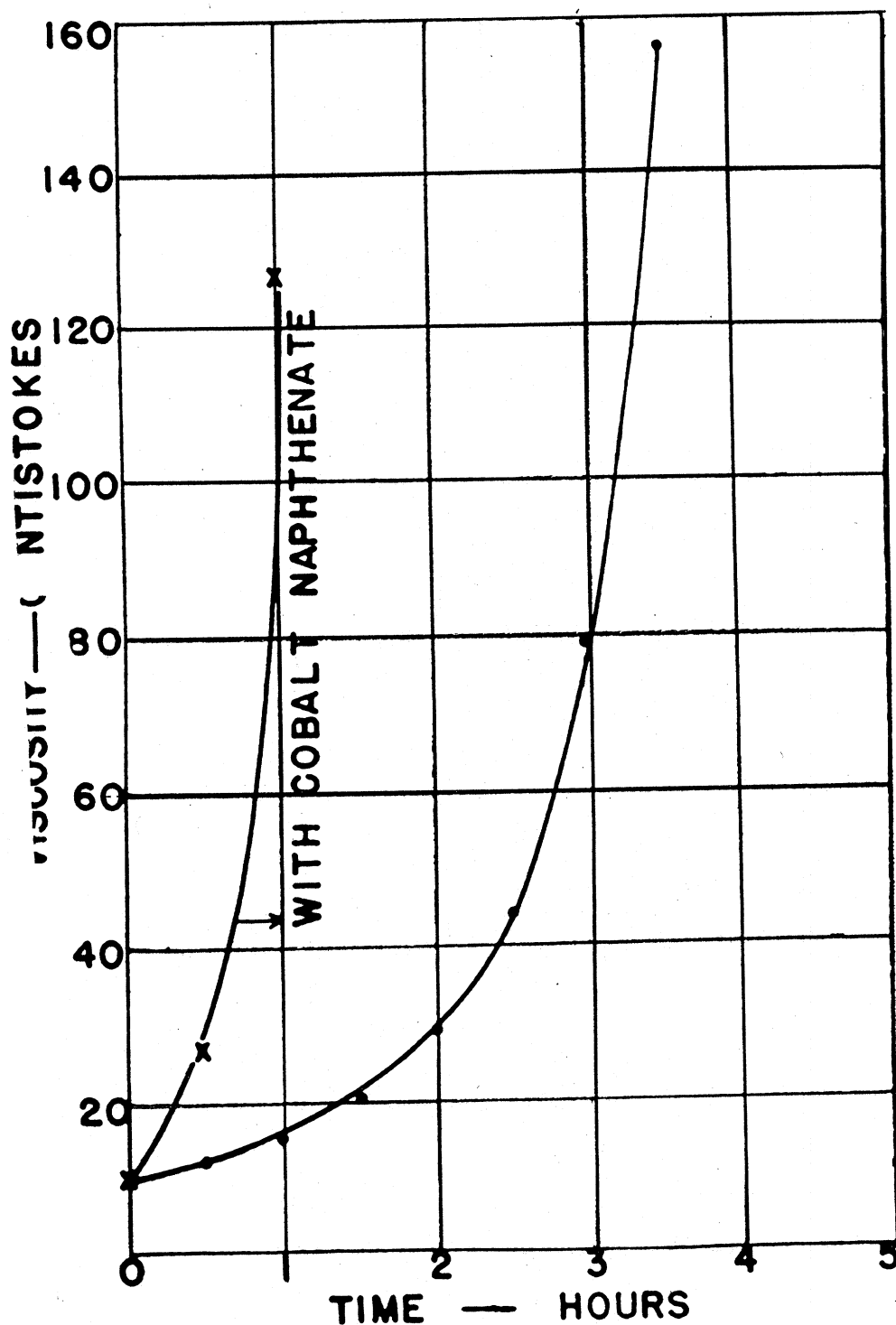# POLYMERIZATION OF ALLYL SUCROSE AT 97°C

FIGURE 1

(vinyl, acrylic, methacrylic and other derivatives) might find a number of useful applications, thus further enhancing the value of sucrose as a raw material for chemical industry.

References

[1] Cox, Gerald J., and Metschl, John. Industrial Uses for Cane Sugar. News Edition. Ind. Eng. Chem. 10, 149-50 (1932).

[2] Criegee, Rudolph, Pilz, Helmut, and Flygare, Horst. Zur Kenntniss der Olefinperoxide. Berichte 72, 1799-1804 (1939).

[3] Engler, C. . Ueber Aktivirung des Sauerstoffs. Berichte 33, 1090-96 (1900).

[4] Farmer, Ernest Harold, and Sundralingam, Alvappillai. The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. I. The Structure and Reactive Tendencies of the Peroxides of Simple Olefins. Jour. Chem. Soc. 1942, 121-39.

[5] Frey, Karl. Ueber die Konstitution der Polysaccharide. Dissertation. Eidgenos. Tech. Hochschule, Zürich 1926, pp. 61.

[6] Long, Louis, Jr. Sugar and Sugar By-products in the Plastic Industry. Scientific Report Series No. 1. Sugar Research Foundation, Inc., New York, April 1945. pp. 62.

[7] Nichols, P. L., Jr., and Yanovsky, E. Preparation and Polymerization of Polyallyl Ethers. Journ. Amer. Chem. Soc. 67, 46-49 (1945).

[8] Nichols, P. L., Jr., Hamilton, R. M., Smith, Lee T., and Yanovsky, E. Allyl Ether of Starch. Ind. Eng. Chem. 37, 201-2 (1945).

Nicolet, Ben H., and Poulter, Thomas C. Epoxy Acids from Oleic and Elaidic Acids. Jour. Amer. Chem. Soc. 52, 1186-91 (1930).

[10] Tomecko, C. G., with Adams, Roger. The Allyl Ethers of Various Carbohydrates. Jour. Amer. Chem. Soc. 45, 2698-2701 (1923).